

Neutron Inelastic Scattering Investigation of Water and Ionic Solutions

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

I. INTRODUCTION

The results of neutron inelastic scattering (NIS) investigations to date on the influence of ionic solutes on the intermolecular vibrations and the diffusive kinetics of the solvent molecules in aqueous solution have been reported in detail in previous annual reports⁽¹⁻³⁾ and in the literature⁽⁴⁻⁶⁾. Only a brief summary is given below:

1) Summary of Previous Results

(a) NIS spectra yield information on vibrational and diffusive motions of H_2O molecules characteristic of the "bulk-solvent" for dilute solutions and characteristic of ion-water complexes for concentrated solutions. At lower concentrations (typically of 0.5 m and below), the torsional components and lower frequency intermolecular modes for the CsCl , NaCl , and MgCl_2 solutions show a pronounced correspondence to those for water. With increasing concentration, this correspondence is lost in a manner specific to the salt. In contrast, any such degree of correspondence to water is not observed for dilute LiCl solutions, except at lower concentrations (typically below about 0.05 m), while for KCl solutions, frequencies characteristic of water persist even to a 4.6 m concentration. The curves of Γ vs. K^2 for dilute solutions are also nearly identical to that for water. This implies that any changes in values of D and τ_0 or in the activation energies are small relative to water. Thus, despite their different hydration powers, the magnesium, sodium, and cesium ions, at concentrations below about 0.5 m, do not strongly disrupt the structure of the distant bulk solvent relative to water. In contrast, LiCl appears relatively more effective and KCl less effective in disrupting the solvent structure.

The ability of such ions to alter the longer-range structure of the solvent depends upon the strength (relative to water) of their primary ion-water interactions, upon the polarization of solvent molecules by the primary complexes, and geometrically upon the degree of structural mismatch between primary hydration complexes and the distant

solvent structure. Both the relative number of H_2O molecules affected and their diffusive freedom depend upon the transition from the distant region, where their ordering and forces are primarily determined by water structure, to the primary hydration complexes, where they are determined by specific ion-water coordinations. Thus, the greater ability of the Li^+ ion to strongly alter the solvent structure at low concentrations could, in part, result from its small number of specifically coordinated primary waters. The H_2O 's adjacent to hydrated Li^+ ions would undergo large reorientations to bond to the hydrated ions, and a cooperative structural readjustment could result. In contrast, larger ions like Na^+ , Mg^{+2} and Cs^+ , which accommodate a greater number of primary hydration waters, would not require as large a structural perturbation. Similar conclusions from the literature are summarized in Table I.

(b) With increasing concentration, the spectral correspondence to water is rapidly lost, and frequencies characteristic of ion-water complexes appear and intensify. Solutions with strongly hydrating ions (e.g., La^{+3} , Mg^{+2} , Li^{+1} and F^{-1}), show intermolecular librational modes and metal-oxygen stretching and bending modes characteristic of ion-water hydration complexes at frequencies similar to those observed in spectra of the correspondening solid salt hydrates. Thus, the strong primary ion-water interactions disrupt the initial solvent structure to form specific ion-water hydration coordinations and the local orderings of H_2O molecules in primary hydration layers of these ions are similar in solution to those present in their solid hydrates. Increasing temperature partially disorders these coordinations and causes these frequencies to broaden.

(c) Solutions of larger, singly-charged cations (e.g., Cs^+ , K^+ and Na^+) also show frequencies characteristic of primary ion-water complexes. Such primary ion-water coordinations, while weaker than those involving small or highly-charged cations, can still be stronger

than the average $\text{H}_2\text{O}-\text{H}_2\text{O}$ bonds in the solvent. Hence, with increasing temperature, $\text{H}_2\text{O}-\text{H}_2\text{O}$ coordinations of the solvent are disrupted, the number of primary hydration waters are increased, and hence their corresponding intermolecular frequencies became sharper and better defined. Similar conclusions obtained by other measurements are summarized in Table II.

(d) The angular and temperature dependence (below 25°C) for the widths of the diffusively broadened incident energy distributions (the "quasi-elastic components") for concentrated solutions are in reasonable accord with the delayed diffusion of individual H_2O molecules. Values of self-diffusion coefficients (D) and of residence times (τ_0) are obtained within error, in agreement with those reported from other techniques⁽⁴⁾. At 1°C , with increasing concentration, the D 's decrease and the τ_0 's increase relative to water for KF , NaCl , LiCl , and MgCl_2 ("positive hydration"), while the reverse is true for CsCl , CsBr , KSCN , KI , KBr and KCl ("negative hydration").

However, for CsCl and CsBr , while the D 's increase and the τ_0 's initially decrease with increasing concentration, they then become nearly constant, due to increased ion-pairing (see Table III). For KSCN solutions, with increasing concentration, D increases and τ_0 decreases initially relative to water. They then go through a maximum and minimum respectively and approach the values for water (corresponding to a decrease in "negative hydration"). Thus, while SCN^- ions increase the diffusive mobility in the solvent, reorientations of H_2O 's in primary hydration coordinations are at least as restricted as those in water.

(e) In concentrated solutions of small and/or highly-charged cations (i.e., Li^+ , Mg^{+2} , La^{+3}), the frequencies and diffusive parameters are primarily determined by the cation and only secondarily by -1 anions. In contrast to the above behavior, for solutions of larger, singly-

charged cations the intermolecular frequencies and the diffusive kinetics show a strong dependence on anion. Thus, in potassium halide solutions, the "structure-breaking" influence of the anions increases as $\text{Cl}^- < \text{Br}^- < \text{I}^-$, and F^- acts as a "structure-maker."

2) Description of Recent Investigations and Review of Background Information

During the contract year 1969-1970, emphasis has been placed on the following areas:

(a) The effects of strongly hydrating anions have been studied in order to further obtain information on anion hydration and its effect on the cation hydration. Thus, a CsF solution has been measured and the results have been compared with those of a CsCl solution. In addition, the $\text{SO}_4^{=}$ anion has been studied in Na_2SO_4 and MgSO_4 solutions in order to compare with the corresponding chloride solutions.

(b) The different components contributing to the diffusive motions in ionic solutions and their relationship to glass formation have been investigated. For this purpose, the spectra of solutions of concentrated LiCl , LiNO_3 , CrCl_3 , $\text{Cr}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3$ have been measured and intercompared. Direct evidence has been obtained for the contribution of diffusive motions other than the activated jumps of individual H_2O molecules to the transport in ionic solutions and their fundamental relationship to the formation of glasses upon supercooling. Such results serve to complement and support the following results of studies on glass transitions and on transport phenomena by Angell et al^(7,8) (under contract with the Office of Saline Water -- see Table IV).

Upon supercooling, aqueous solutions of many multivalent ions become increasingly viscous and, below a characteristic temperature (T_g), form solid glasses⁽⁸⁾. It has been suggested that with decreasing temperature, "liquid-like" diffusive motions become damped as T_g is approached, and a behavior akin to a harmonic solid is approached. From Raman spectra it has been suggested⁽⁹⁾ that the formation of strongly coordinated, centrosymmetric cation-water complexes may in part

inhibit the formation of crystalline ice and favor glass formation. Recently, Angell and Sare⁽⁸⁾ have studied the dependence of T_g on cation, on anion, and on concentration and have found that for a given concentration and anion, the value of T_g increases with cationic charge. For a given cation, the variations in T_g with anion are large, and T_g increases in the progression: chloride < nitrate < sulfate (hence, with the basicity of the anion). Further, solutions containing quasi-spherical, singly-charged anions have, in general, lower T_g 's, while those containing asymmetric anions have higher T_g 's. This dependence was attributed to the bonding of the anions to the H_2O molecules in the cation hydration sheath. It was suggested that the anions thus order their environment, reduce the configuration entropy, and raise T_g .

For salts with a common anion and cation charge, the T_g 's decrease linearly with concentration to a point such that they become independent of the cation and then approach the T_g for vitreous ice. A concentration is then reached below which the cations become effectively shielded by their hydration sheaths, which correspond to approximately 6 to 8 H_2O molecules for LiCl, 17 to 20 H_2O molecules for divalent cations, and 24 to 31 H_2O molecules for trivalent cations. Further, Angell and Sare⁽⁸⁾ argued that chloride solutions at low temperatures tend to separate into "salt-rich" and "solvent-rich" regions. In the former, H_2O molecules and anions may be oriented about cations with local orderings like those of the corresponding solid salt hydrates. Similar conclusions have been reached from observed Raman⁽¹⁰⁾ and neutron inelastic scattering (NIS) investigations⁽⁴⁾ of concentrated ionic solutions made at temperatures above 1°C. In contrast, according to Angell and Sare⁽⁸⁾, the observed dependence of the T_g 's on concentration for nitrate solutions did not indicate such a phase separation.

In NIS investigations, the spectra for solutions, glasses and solid salt hydrates were measured by neutron inelastic scattering in order to provide information at a molecular level to complement the

measurements on T_g discussed above. In addition, it might be expected that any ordering involving the ion-water complexes could be similar in the glass and in the supercooled liquid, and any effects arising from the coupling of such complexes to a lattice (as for the solid salt hydrates) would be absent. Also, in the supercooled liquid, relaxational broadening would be reduced relative to temperature above 1°C (where most previous measurements on water and ionic solutions have been made), which should facilitate comparisons between the spectra of the supercooled solutions and the glasses.

(c) Ternary Solutions:

Neutron scattering studies on single salt solutions have been extended to study the changes in the hydration of ions and in the associated diffusive kinetics of H_2O molecules that occur upon the mixing of two solutions. To date, such measurements have been made for 4.6 m NaCl - 4.6 m LiCl, 4.6 m NaCl - 1.0 m MgCl_2 , 4.6 m NaCl - 2.2 m MgSO_4 , 4.6 m NaCl - 1.0 m Na_2SO_4 and 4.6 m NaCl + 4.6 m CsCl solutions.

From measurements of the thermodynamics, of viscosity, and of "salting-out" it has been argued that in solutions containing more than one salt the combined structure-making and -breaking effects of ions are not additive. Further, both experiment and theory have implied that, upon mixing, significant changes in the hydrations of the ions present, in the diffusive kinetics and in the structure of the solvent, can occur. Thus, Wood et al⁽¹¹⁻¹⁶⁾ have studied the heats of mixing for aqueous ternary solutions and have concluded that:

1. The orientations of the water molecules about the ions and the changes that result upon mixing are important in determining whether the heat of mixing is endothermic or exothermic. The heat of mixing appears to depend upon the detailed hydration structure and the electrostrictive properties of the ion which, in turn, depend simultaneously upon ionic size, charge and concentration.

2. For consideration of the heats of mixing, it was convenient to divide ions into the "structure-making" or "positively hydrating" ions (e.g., Li^+ , Na^+ , Mg^{+2} , Ca^{+2} , Ba^{+2} , F^-) and the "structure-breaking" or "negatively hydrating" ions (e.g., K^+ , Rb^+ , Cs^+ , Br^- , and Cl^-). The heat of mixing is endothermic within the same group and exothermic between different groups.

Recently, based upon his previous theory of the hydration of ions in solution, Samoilov⁽¹⁷⁻¹⁸⁾ has proposed a semi-quantitative theory which attempts to account for observed changes and trends in ion hydration in mixed salt solutions, and for salting-out phenomena at a molecular level. While, as yet, this theory is largely qualitative, it does appear to correlate with many of the observed dependences of the heats of solution and of mixing upon the changes in the hydration of individual ions that occur upon mixing, the cation and anion sizes and charges, concentration, and temperature. Such predictions of this theory can also be tested directly at a molecular level by measurements such as NIS that provide information concerning changes in the bonding and orientation of H_2O molecules in the hydration sheaths of ions, and corresponding changes in the diffusive kinetics and mobility of H_2O molecules that would occur upon mixing.

II. EXPERIMENTAL

The measurements were made using a beryllium filtered incident beam and a neutron time-of-flight spectrometer described previously⁽¹⁴⁾. General descriptions of this type of spectrometer and its applications to studies of liquids are in the literature⁽¹⁹⁾. The samples of the solutions (prepared from analytical-grade reagents and deionized water) were contained in grooves of average thickness of 0.42 mm in an aluminum plate backed by a flat piece of cadmium. A 2μ layer of an inert polymer film protected against corrosion, and the cell was shielded with cadmium to prevent scattering by the sample holder. As reported previously⁽²⁰⁾, the polymer film and the aluminum window gave negligible spectral

distortions or background contributions and the sample thickness used gave negligible spectral contributions due to multiple scattering. For the spectra taken at 274°K, the sample was cooled by circulating water from an ice-water bath, appropriately shielded to avoid the scattering of neutrons by the coolant.

The procedures used for the treatment of the data, for checking their reliability and reproducibility, and for the analysis of the quasi-elastic components have been extensively described in previous papers⁽²⁰⁾ and only a summary is given below.

The observed spectra were corrected for background, counter-efficiency, and chopper transmission. The background corrections were made by a channel-by-channel subtraction of spectra obtained for the empty sample holder. The background was predominantly a flat component upon which was superimposed a weaker, broad distribution centering at about channel 146. The latter component varied with rotor speed as expected for the "180° burst." Small, but significant, variations occurred in the background with scattering angle and cell geometry, but spectra independent of a given cell could be systematically obtained after background corrections. Typical statistical uncertainties are shown with the reported spectra and correspond to plus or minus one standard deviation as calculated from the total number of background counts-per-channel. The solid curves in the neutron spectra were averaged through the data points with regard to the statistical uncertainties. Where a singularity was marginal in intensity with regard to statistical error, it was assigned only if it was systematically reproduced at more than one scattering angle, temperature, and concentration. In addition to statistical considerations, the reproducibility and reliability of spectral features were tested by (a) comparisons of spectra remeasured with fresh solutions, (b) comparisons of spectra for different scattering angles and for different temperatures, (c) comparisons of data collected on the four independent counter banks, electronics, and memory banks of the time-of-flight analyzer, and (d) comparisons with background spectra for the empty cell to show that no spectral features arose from neutrons scattered by the sample holder or shielding.

III. RESULTS AND DISCUSSION

1) Anion Effects

The effects of strongly hydrating anions (F^- and SO_4^{2-}) have been studied to obtain further information on anion hydration and its influence on cation hydration. As discussed above, most previous work involved singly-charged anions and their relative influence (e.g., Cl^- vs. NO_3^-). During the present year, measurements on a cesium fluoride solution were compared with those obtained previously for cesium chloride and cesium bromide, and measurements on Na_2SO_4 and $MgSO_4$ solutions were compared with those for the corresponding chloride solutions. A number of the effects typically observed for anions in aqueous solutions are summarized briefly in Table III. It can be seen that the following general trends for the influence of anions should be considered.

(a) In the case of strongly hydrating cations, large -1 anions (as discussed above) play a minor role. The ion-water coordinations, the self-diffusion coefficients, and the residence times are primarily determined by the cations. However, as the anion "strength" is increased, the anion may more readily approach the primary hydration layer, disorder the orientation of the primary water molecules, and decrease their residence times. One should consider this as "indirect ion-pairing" on a "time average" as the anion need not necessarily pair directly with the cation but may only simply approach it and spend an average time in this vicinity during which time its field and coordination to the hydration waters may cause such effects. Large +1 ions which form much weaker primary water coordinations are more susceptible to direct ion-pairing; thus, for example, for the cesium ion a number of experiments have reported⁽²¹⁾ the presence of direct ion-pairing and that this increases in passing from iodide to bromide to chloride (e.g., with increasing charge-to-radius of the cation and anion).

(b) The temperature may also influence ion-pairing. Thus, as the temperature is decreased, the anions which attempt to approach the cation on a time-average are forced further away as the primary hydration layer becomes more stable⁽⁹⁾.

(c) Any degree of direct ion-pairing may effectively dehydrate the cation and strongly reduce the residence times and strength of bonding of any remnant primary waters⁽²²⁾.

(d) Where strongly coordinated cation-water complexes exist, such that diffusive motions involve both the transfer of the individual water molecules and the diffusion of hydrated ions together with the hydration layers, with increasing basicity anions may, in general, restrict the diffusive motions associated with the hydration complexes⁽⁸⁾. This behavior and its relationship to glass formation will be discussed in more detail below.

(e) In the formulation of his theory for the interactions of two salts in ternary solutions, Samoilov⁽¹⁷⁻¹⁸⁾ (as detailed below) has argued that with increasing hydration strength the anions tend to "salt-in" or stabilize water molecules around the cations. Samoilov's theory does not take into account direct ion-pairing and, thus, the water molecules that are being stabilized may well be those in second and higher hydration layers. Samoilov argues that the stabilization results from the strengthening of the potential between the primary cation-water coordinations together with a dipole field interaction whereby the hydrated anion interacts with the electric moments of the water molecules in the primary hydration layers of the cations, and serves to stabilize them against reorientations.

(f) In the presence of a strongly hydrating anion, i.e., F^- or SO_4^{2-} , and a weakly hydrating cation, it must also be questioned which ion, if any, dominates in determining the ordering of the water molecules. Thus, in an approximate sense, the strongly hydrating anions may orient water molecules around them, and then, in turn, the hydrated anions may pack around the weaker cations. A similar question for the inverse case has been raised by Brady⁽²³⁾ who questions whether the chloride hydration is indeed a true one in lithium chloride solutions. Rather, he suggests that the lithium ions may strongly coordinate water molecules toward them, and then these hydrated complexes in turn pack around the chloride ions.

The results of our investigations to date may be summarized as follows:

A. CsF Solutions. Previously⁽⁶⁾ it has been shown that both cesium chloride and cesium bromide act as "negative hydrators," increasing the self-diffusion coefficient and decreasing the residence times for water molecules relative to pure water. In addition, it was noted that while the cesium ion serves to disrupt the water structure and decrease the activation energy, defined primary ion-water coordinations exist with the Cs^+ ion. Thus, the NIS inelastic spectra for both concentrated CsBr and CsCl solutions showed similar frequencies characteristic of the primary cesium ion-water coordinations. However, the larger Br^- ion (relative to the Cl^-) disrupted the water structure and allowed the Cs^+ ion to more fully hydrate at a lower concentration. At higher concentrations the values of the self-diffusion coefficients and residence times for both of these salts tended to "saturate" due to the effects of increased ion-pairing and approached nearly equal values for the two salts (being approximately independent of anion and being primarily dependent on the cesium ion-water coordinations).

In contrast, the spectrum for CsF shows marked variations from the above two salts. In Figure 1, the spectra for a 4.6 m solution of CsF are compared with spectra for $\text{KF} \cdot 2\text{H}_2\text{O}$ and for a 4.6 m solution of KF . In Figure 2, the curve of Γ vs. K^2 , obtained from the analysis of the quasi-elastic component, is also shown. Previously^(4,6) it was shown that with increasing concentration the inelastic frequencies for a KF solution departed from those of water and closely approached those of $\text{KF} \cdot 2\text{H}_2\text{O}$, indicating the formation of local ion-water primary complexes similar to those in the solid salt. In Figure 1, it is seen that the inelastic frequencies for the CsF show no similarities within resolution to those observed previously for CsBr and CsCl , but rather correspond strongly to those observed for the KF solutions and for $\text{KF} \cdot 2\text{H}_2\text{O}$. Thus, in the presence of larger, singly-charged cations, the F^- anion appears to dominate and to determine the coordinations of the primary water and the relative influence of the cations appears secondary, at best. In keeping with this behavior it is seen that CsF has decreased the self-diffusion coefficient and increased the residence time relative

to water, thus acting as a positive hydrator, while CsBr and CsCl, as noted previously, acted as strong "negative hydrators."

Danford et al.⁽²⁴⁾ have recently argued from x-ray diffraction results on NH_4F solutions that the ammonium ion is able to incorporate into and stabilize the water structure, while the small fluoride ion is unable to sterically disrupt the water structure and goes into an interstitial position. Further, Brady⁽²⁵⁾ has argued that the K^+ ion (being about the same size as a water molecule and having a low charge) is unable to strongly disrupt water structure and may actually incorporate into it. However, unlike the ammonium fluoride case, it is clear that KF can break down existing water structures and form strong ion-water complexes. In the case of ammonium fluoride, it appears that the ammonium ion substituting into the water structure has stabilized it sufficiently to prevent the field of the fluoride ion from disrupting it. However, for KF the K^+ cation would not promote such a stabilization and the field of the fluoride ion would be sufficient to further disrupt the water structure. In a CsF solution, the large Cs^+ ion would even more readily disrupt and break the water structure than the K^+ cation, allowing the fluoride ion to hydrate more readily. While the curve of Γ vs. K^2 for CsF lies well below those for CsBr, CsCl and water, it does not appear to be as strong a positive hydrator as KF due in part to the influence of the cations. X-ray diffraction data⁽²⁶⁾ have shown that in $\text{KF} \cdot 2\text{H}_2\text{O}$ each potassium has six close neighbors, two of which are fluorides -- the fluorides being hydrogen-bonded to waters in the primary coordination spheres of the cation. However, Lawrence and Kruh⁽²¹⁾ have argued that in cesium salts ion-pairing occurs, and that the degree of ion-pairing should increase with decreasing size of the anion. Thus, while fluoride-water coordinations may be as strong as those of cesium fluoride and potassium fluoride, ion-pairing may have reduced their relative number in the former solution, and thus effectively increased the self-diffusion coefficient and decreased the residence time, τ_0 , for water molecules relative to potassium fluoride.

B. MgSO₄ and Na₂SO₄ Solutions. As previously reported⁽⁴⁾, the spectra of solutions containing small and/or highly-charged ions show well-defined primary ion-water frequencies similar to those observed in the corresponding solid state hydrates. It was shown that for solutions of lanthanum and lithium salts both the primary ion-water frequencies and the curves of Γ vs. K^2 are only slightly changed when chloride ions are replaced by nitrate ions, indicating that both the ion-water coordinations and the diffusive kinetics are primarily determined by the cations. In Figures 1 and 2, the spectra and the curves of Γ vs. K^2 are compared for a 2.2 m solution of MgSO₄ and a 4.6 m MgCl₂ solution. The Γ vs. K^2 for the more dilute 2.2 m solution of MgSO₄ lies slightly below that for a 4.6 m solution of MgCl₂. Thus, the sulfate ion has further decreased the self-diffusion coefficient and increased the residence time in the magnesium sulfate solution (relative to the magnesium chloride), and hence effectively increased the "positive hydration." However, for both the magnesium sulfate solution and its corresponding solid salt hydrate, the frequencies in the region of librational modes of H₂O molecules coordinated to the cation are similar to those observed in magnesium chloride, indicating that a degree of similarity in the primary cation-water coordinations persists. However, at lower frequencies where the hydrogen bond stretching modes are typically observed, spectral differences occur. These results can be readily understood by consideration of the reported structures and local orderings obtained from x-ray diffraction for a large number of magnesium salt hydrates. For many magnesium salt hydrates (MgCl₂·6H₂O, MgBr₂·6H₂O, Mg(ClO₄)₂·6H₂O, MgS₂O₃·6H₂O)⁽²⁶⁾ the magnesium ion is always surrounded octahedrally by six water molecules with cation-water distances typically ranging between 2 and 2.2 Å. However, for Mg₃(PO₄)₂·8H₂O where the magnesium is again surrounded octahedrally by oxygens, the coordinations consist of some waters and some oxygens from the phosphate groups. Thus, it would appear that the similarity in the inelastic frequencies observed for the magnesium chloride and the magnesium sulfate solutions may primarily reflect a

tendency of the magnesium ion to be octahedrally coordinated to $6\text{H}_2\text{O}$ molecules in the primary layer. Further, the reported⁽²⁶⁾ crystal structure for magnesium sulfate heptahydrate shows that the magnesium ion is again octahedrally coordinated. The extra H_2O molecule is not coordinated to a metal atom, but instead occupies a hole in a structure of primary hydration octahedra and SO_4 tetrahedra. In magnesium sulfate tetrahydrate the magnesium atoms are again octahedrally coordinated with oxygens; however, four of these oxygens belong to water molecules and two to sulfate groups. Thus, in a 2.2 m solution of magnesium sulfate (where there are approximately 24 water molecules per ion pair) six of the water molecules could be expected to octahedrally surround the magnesium cation; the remaining water molecules in principle could be distributed between sulfate groups and the second hydration layer of the magnesium ion. However, the fact that the Γ vs. K^2 curve for the 2.2 m solution of magnesium sulfate lies lower than that for an equivalent concentration of magnesium chloride indicates that the sulfate ion serves to decrease the self-diffusion coefficient and increase the residence time of such H_2O 's in the high hydration layers of the cation. Thus, the sulfate groups do not serve solely to bridge $\text{Mg}(\text{H}_2\text{O})_6^{+2}$ octahedra, but affect quite a number of H_2O molecules without contributing significantly to the spectral features of specific anionic coordinations.

Further evidence is obtained from the spectrum of a Na_2SO_4 solution. The inelastic frequencies in the spectrum of a Na_2SO_4 solution are very similar to those of a NaCl solution (Fig. 3). It must be pointed out that ordinarily the Na^+ ion is generally considered to be a weak structure-making cation. However, it has been reported that in $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ the sodium atoms have six water neighbors with a slightly distorted octahedral coordination, indicating that the cation has a uniquely coordinated hydration sheath. In addition, the Γ vs. K^2 curve for a 1 m Na_2SO_4 solution lies well below that of a 4.6 m NaCl solution, again showing that the $\text{SO}_4^{=}$ serves to decrease the self-diffusion coefficient and increase the residence time of the H_2O 's. These results support the argument that the $\text{SO}_4^{=}$ ion enhances the hydration of the cations. Thus,

neglecting the absence of direct ion-pairing, Samoilov^(17,18) has pointed out that the hydration of the cation is increased by the anions due to the decrease in disorientated water molecules about the cation. This hydrating effect increases with increasing charge of the anion. However, this effect also depends upon the hydrating strength of the cation⁽²⁷⁾. For a highly charged cation the tendency for direct ion-pairing with an anion would reduce the cation hydration. Thus, at high enough temperatures, NMR measurements of solutions of rare earth sulfates⁽²²⁾ showed that the cations pair with the $\text{SO}_4^{=}$ ion. X-ray diffraction measurements on $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ⁽²⁶⁾ also show that in contrast to $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the $\text{SO}_4^{=}$ ion closely surrounds the La^{+3} ion and keeps the H_2O 's away. This interpretation agrees well with the NIS observations on the effects of the $\text{SO}_4^{=}$ ion, and may probably predict the effect of the $\text{SO}_4^{=}$ in rare-earth sulfate solutions which we have not measured.

2) Diffusive Motions of Hydrated Ions and Their Relationship to Glass Formation

A. The Dependence of the "Quasi-elastic" Component on the Nature of the Diffusion Processes.

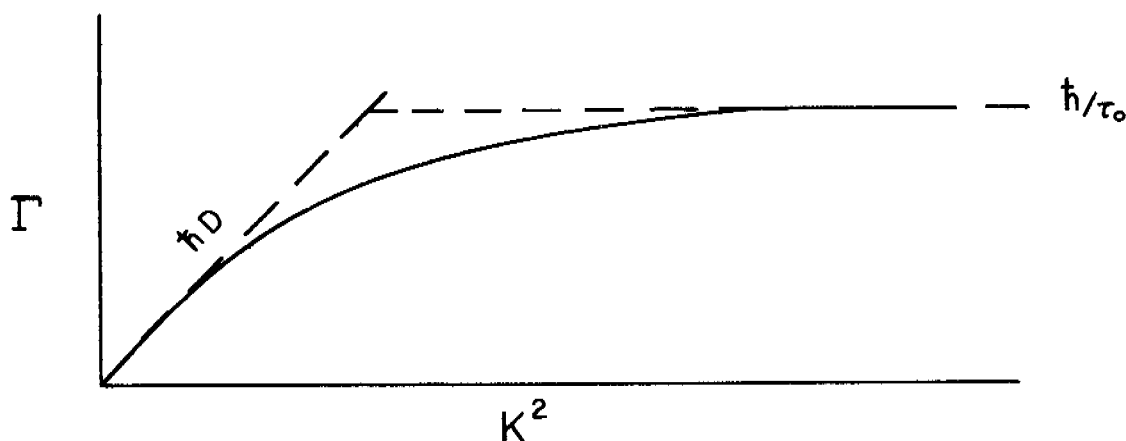
As discussed previously in detail, at lower temperatures (typically below 25°C) the angular dependences and temperature dependences of widths, gamma, and areas of the observed quasi-elastic maxima are in accord with a simple delayed diffusion behavior⁽²⁸⁾. However, a jump-diffusion model, in general, constitutes only an approximation as it does not go to the short time or limit properly, as required for any complete correlation function. However, at lower temperatures significant contributions from such free-particle motions would not occur until very short times (corresponding to high K^2 values) are reached, and hence, if the delay times, τ_0 , are long, a simple delayed diffusion constitutes an adequate approximation. For this model the width and the area and their dependences on K^2 are as follows:

$$\Gamma = \frac{\hbar}{\tau_0} \left[1 - \frac{e^{-1/6} \langle \mu^2 \rangle K^2}{1 + K^2 \tau_0 D} \right] \quad \ln A = C - \frac{K^2 \langle \mu^2 \rangle}{6}$$

H₂O vibrates for period (τ_0) and diffuses for time (τ_1) such that ($\tau_0 \gg \tau_1$) over length $\langle l^2 \rangle$. Then:

$$D = \frac{1}{6} \frac{\langle l^2 \rangle + \langle \mu^2 \rangle}{\tau_0 + \tau_1} \longrightarrow \frac{1}{6} \frac{\langle l^2 \rangle}{\tau_0}$$

The dependence of the width Γ on K^2 is shown schematically below:



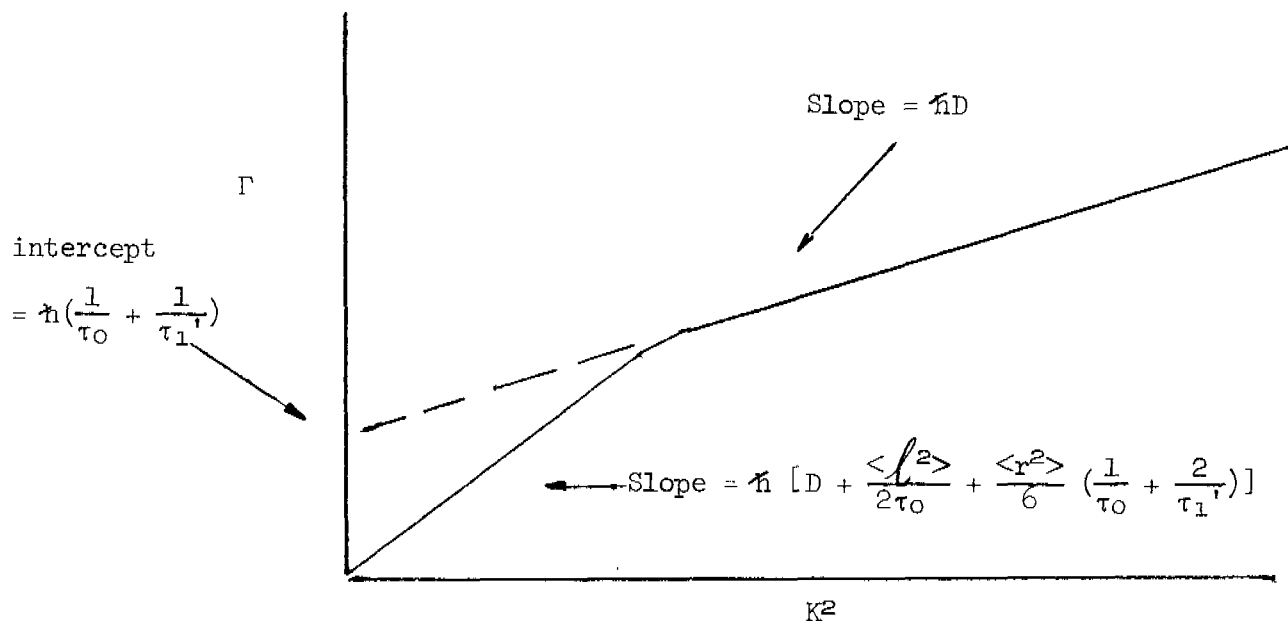
It should be noted that the curve of Γ vs. K^2 initially rises linearly with the slope given by $\hbar D$ as expected for long interaction times where the diffusive kinetics should be characteristic of classical diffusion. At shorter times (i.e., larger values of K^2), the curve approaches asymptotically the value of \hbar/τ_0 . In reality, however, at some higher value of K^2 , the curve must rise again in accord with a "free particle" behavior for which the simple jump diffusion model, shown above, does not account. However, as can be seen by reference to the data of Fig. 4, and, in particular, to the curve of Γ vs. K^2 for 3.5 m LaCl₃ and 5.7 m MgCl₂ solutions, a good approximation of this jump diffusion behavior within the observed range of K^2 is achieved at lower temperatures.

More generally, in order to calculate a broadening for the quasi-elastic maxima that would arise where contributions both from motions of hydrated cations and from the exchange of primary waters could occur, it is useful to consider a model derived by K. E. Larsson and L. Bergstedt⁽²⁹⁾. It assumes that a protonic group may vibrate on a center of mass of a larger molecule for a time τ_0 and then jump a characteristic distance l in a time τ_1 . In correspondence, the center of mass of a larger molecule carrying the protonic group may vibrate for a time τ_0' time, and then undergo diffusion characterized by a self-diffusion coefficient, D , for a time τ_1' . The most general expression obtained is complex. However, certain simplifying assumptions can be made which are in keeping with what might be expected for ionic solutions containing strongly hydrated cations at high concentrations. If it is assumed that the times τ_0 and τ_1' are much larger than the characteristic period time τ_0' , then the expression for Γ vs. K^2 is again a Lorentzian and the value of the width for small and large K^2 values is given below:

If $\tau_1', \tau_0 \gg \tau_0'$,

$$\text{Then, for } K^2 \text{ Small } \Gamma \approx \hbar \left[D + \frac{\langle l^2 \rangle}{2\tau_0} + \frac{\langle r_1^2 \rangle}{6} \left(\frac{1}{\tau_0} + \frac{2}{\tau_1'} \right) \right] K^2$$

$$\text{Then, for } K^2 \text{ Large } \Gamma \approx \hbar \left[DK^2 + \frac{1}{\tau_0} + \frac{1}{\tau_1'} \right]$$



As for the simple jump diffusion model, Γ is again linear in K^2 for small values. However, the slope now involves both the self-diffusion coefficient, D , for the center of mass, and the effective self-diffusion coefficient $\ell^2/2\tau_0$ for the protonic group, as well as a third factor depending upon the amplitude. However, in contrast to the simple jump diffusion model, at large values of K^2 , a constant value is not approached. Rather, a different curve again rises linearly but with a different slope which is simply $\ell^2 D$. In the above model it has been assumed that τ_0 and τ_1' time are of the same order of magnitude. This might be a realistic approximation if the residence times for the H_2O molecules were sufficiently short so that they occurred within the neutron interaction time, but yet were sufficiently long so that the waters of hydration could diffuse part of the time with the cations. As shown in Figure 5, evidence of such a double slope behavior is observed for 10 m solutions of $LiCl$ and $LiNO_3$ and may reflect motions of H_2O molecules in the second hydration layer, which could exchange within the neutron interaction period but also more with the cation part of the time.

Further, if it is assumed that the limit is approached whereby

$$D \gg \left[\frac{\langle l^2 \rangle}{2\tau_0} + \frac{\langle r_j^2 \rangle}{6} \left(\frac{1}{\tau_0} + \frac{2}{\tau_1'} \right) \right]$$

and

$$DK^2 \gg \left(\frac{1}{\tau_0} + \frac{1}{\tau_1'} \right),$$

then

$$\Gamma \longrightarrow \ell^2 DK^2 \text{ and is linear in } K^2 \text{ over the entire range.}$$

Indeed, as shown in Figure 4, such a simple straight-line behavior involving a low value of D is observed for 15 m $LiCl$ and for concentrated $CrCl_3$ and $Cr(NO_3)_3$ solutions. Here the observed quasi-elastic maxima and its broadening is then primarily characteristic of motions of the hydrated cation as a whole. The residence times for the exchange of primary waters of hydration is longer than the neutron interaction time of 10^{-11} - 10^{-13} (see Table IV) and the time τ_1' that the center of mass is unbonded

is long compared to any period τ_0' that it is bonded, and also long compared to neutron interaction time. Under such conditions, the broadened quasi-elastic maxima would be dominated primarily by the diffusive motions of the hydrated ions and would rise nearly linearly with the slope proportional to D.

The question arises as to the type of motions that the centers of mass undergo and how they depend functionally on the motions of the hydrated ions, as described in terms of Langevin's equation^(30,19):

$$1) \quad M\ddot{\mathbf{r}} + M\xi\dot{\mathbf{r}} = \mathbf{F}(\tau) \quad \text{where } \mathbf{F}(\tau) \text{ is a rapidly varying Stochastic Force} \quad (1)$$

$$2) \quad \text{where } D = \frac{kT}{M\xi} \quad (2)$$

ξ is the friction coefficient and $1/\xi$ is, in essence, to be considered as a short delay time before diffusion sets in. As pointed out by Larsson⁽³¹⁾, it is a measure of the collision time itself. In addition, the above relation for the self-diffusion coefficient predicts that it should be inversely proportional to the mass. A comparison of the curves of Γ vs. K^2 for 15 m LiCl and 4.23 m CrCl₃ solutions shows that although the CrCl₃ is more dilute, the Γ vs. K^2 is also linear and indeed has a smaller slope, corresponding to a smaller value of the self-diffusion coefficient. Just such a behavior would be expected in view of the heavier mass of the chromium hydration complex relative to the primary lithium hydration complex. If the assumption is made that all the water molecules present are moving with the cations, then the ratio of the masses of the hydration complexes ($M_{\text{Cr}}/M_{\text{Li}}$) obtained would be equal to 3.62 and the observed ratio of the D's (Li/Cr) is equal to 4.28. Hence, to the first approximation, the majority of the change in the self-diffusion coefficient in going from the lithium to the chromium solution can be accounted for in terms of just the expected change in the mass of the hydrated cations, in accord with Eq. 2 above. Values for $1/\xi$ of 6.26×10^{-15} and 5.31×10^{-15} sec. respectively are obtained for the lithium and chromium solutions.

As shown by Larsson, one can define an interaction time $\tau_{\text{obs}}^2 = M/K^2kT$. If the neutron is to observe a classical diffusion

behavior it is then required that $(1/\xi)/(\tau_{\text{obs}})$ is much less than unity. Using the above values for $1/\xi$, the masses, the temperatures, and the largest available values of K^2 , it is indeed seen that this ratio would be less than unity throughout our entire observation range of K^2 and, thus, a classical diffusion behavior as observed could logically and consistently be expected. Further, a value of the self-diffusion coefficient has been reported⁽³²⁾ for the motion of the $\text{Cd}(\text{H}_2\text{O})_4^{+2}$ complex in melts of salt hydrates. If, using the reported value of D and the mass of this complex, a value of $1/\xi$ is calculated, it is of the order of magnitude of the characteristic times observed in the present neutron experiments, as reported in Table IV. NMR investigations⁽³³⁾ have reported a possible reorientation involving the hydrated lithium ion in aqueous solutions. A correlation time of the order of 10^{-11} has been reported from the NMR data and can be compared to the present data. The NMR correlation time, τ_c , is given by

$$\tau_c = \frac{\eta_0 V_m}{kT} \quad (3)$$

where V_m is the volume of the hydrated ion and η is the viscosity. Then, from the formula⁽¹⁹⁾

$$\eta = \frac{kT}{2R_g D} \quad (4)$$

and the Stokes-Einstein relationship in Eq. (2) above, the following relation is obtained between the correlation function and the friction coefficient:

$$\tau_c = \frac{M^* V_m \xi}{2R_g kT} \quad (5)$$

If the values of ξ , the friction coefficient from the neutron spectra (as given above), are used together with reasonable values of the masses and the radii of the hydration complexes, a value of τ_c typically equal to 10^{-10} secs. is obtained for the lithium hydration complex. The order

of magnitude is in reasonable agreement with reported values from the NMR experiments.

As noted above, in contrast to the behavior observed for the simple jump diffusion cases, the more basic anions (i.e., NO_3^- relative to Cl^-) serve to decrease the observed self-diffusion coefficient associated with the hydration complex. It would appear that the more basic anion may be effectively increasing the friction coefficient, ξ , a picture which would be in accord with suggestions (discussed below) by Angell and Sare⁽⁸⁾ that anions may bridge the hydrated cations and further restrict their motions. While such a picture must be considered as tentative at present, Zitseva and Fisher⁽³⁴⁾ have proposed a hydrodynamic theory for the motion of ions in solution taking into account the effect of ion hydration. They derive a complex expression for the product of the mass and friction coefficient, as appears in the Stokes-Einstein relationship for the self-diffusion coefficient, which depends upon the coefficients of both the shear and volume viscosities as well as the potential describing the cation-water forces holding the hydration shells. Both the "effective mass" and the friction coefficient depend upon these primary cation-water interactions, since both the time average number of waters moving with the cation and the strength of the interactions between the hydration sphere and the anions would be strongly determined by the primary water-ion interactions. Thus, these authors argue that as such interactions become weaker and H_2O molecules may exchange more rapidly between the hydration layers and the solvent, both the effective mass and ξ must decrease.

B. Discussion of Results and Their Relationship to Glass Formation

In the above formulation, it has been assumed that scattering law was in accord with a correlation function obtained by the classical formulation of the Langevin equation. Further, the curves of Γ vs. K^2 were interpreted to be in accord with the long time limit

$$\frac{\tau_{\text{obs}}}{\tau_B} \gg 1,$$

in accord with a classical diffusive behavior with

$$D = \frac{kT}{M\xi} = \frac{kT}{M} \tau_B \quad (6)$$

However, in the quantum mechanical case, recoil effects may also contribute to the observed width for certain values of K^2 . It is therefore necessary to consider the relative contributions of both the intensity and width of each component in order to convincingly assign the Γ vs. K^2 curves to classical diffusion. Vineyard⁽³⁰⁾ has shown that there exists a critical value of

$$K = K_c = \left(\frac{kT}{MD^2} \right)^{1/2} \quad (7)$$

such that:

a) when $K \ll K_c$, the contribution from the recoil term is low and broad, while the diffusive motion gives a high and relatively narrow contribution whose width goes as $\hbar^2 K^2$

b) when $K \gg K_c$, the reverse of (a) is true, with the recoil term giving the predominant contribution, and with an energy shift

$$\omega_0 = \frac{\hbar^2 K^2}{2M} \quad (8)$$

In both (a) and (b) the slope is linear in K^2 , and therefore, for small slopes on Γ vs. K^2 curves, it can be dangerous to assume that an observed linear behavior of Γ vs. K^2 necessarily implies a simple diffusive behavior. If K is taken as K_c such that the recoil effects have significant intensity, then the energy shift:

$$\omega_0 = \frac{\hbar^2}{2M} \frac{kT}{MD^2}; \quad \text{or,} \quad \frac{\omega_0}{kT} = \left(\frac{\hbar}{\tau_B} \right)^2 \frac{1}{(kT)^2} \quad (9)$$

where $\tau = 1/\xi$; the corresponding width, Γ' , is of the order of magnitude of ω_0 . Under such conditions, if quantum effects are not to contribute, then

$$\frac{\Gamma_{\text{obs}}}{kT} \gg \frac{\Gamma'}{kT}, \text{ which may not be true for small values of } M, \text{ of } D, \text{ or of } \tau_B.$$

In the present experiment the range of K^2 was such that $0 \leq K^2 \leq 5 \text{ (\AA}^{-2}\text{)}$. The smallest value of M involved was $\sim 80 \text{ A.M.U.}$ (for 15 m LiCl) and the values of D involved were of the order of $10^{-5} \text{ cm}^2/\text{sec}$. Hence, in the range of the present experiment $K^2 \ll K_c^2$ and recoil effects should be negligible. In like manner, $\Gamma \approx 8 \times 10^{+2} \text{ mev}$, hence, $\Gamma_{\text{obs}} \ll \Gamma'$, and any contribution of the recoil effects would give rise to a broad contribution relative to Γ_{obs} .

It has been suggested that the diffusive motions of hydrated cations and their restriction with decreasing temperature and with increasing anion basicity may be intimately related to the formation of glasses. To investigate this problem, concentrated solutions of lithium chloride, lithium nitrate, chromium chloride, chromium nitrate and lanthanum nitrate have been investigated. The concentrations and salts were selected for the forthcoming reasons. For most of these salts, solubility allowed concentrations to be reached such that the majority of the water molecules present would be expected to be strongly coordinated in the primary hydration layers of the cations. In such primary layers, the exchange times for the water molecules undergoing individual jumps would be expected (see, for example, Table IV) to exceed neutron interaction time (10^{-11} , 10^{-13} sec.). Such motions would not be expected to contribute to the neutron spectra, which would then be characteristic of motions involving hydration complexes if they occurred many times during the interaction time. Evidence has been cited in the literature (Table IV) to indicate that diffusive motions of cations together with their waters of hydration may also contribute to the overall diffusive kinetics as well as the jump diffusion of individual water molecules. In addition, at these concentrations, solutions of these salts could be held in a supercooled condition so that spectral measurements could be made both upon the supercooled liquid above the glass transition temperature and below the glass transition temperature.

Both the nitrate and chloride solutions were run since, as noted above, the variation between a chloride and a nitrate ion makes only a small change in the parameters characteristic of the jump diffusion of individual water molecules. In contrast, Angell et al.⁽⁸⁾ have shown that the more basic nitrate ion can increase the glass transition strongly relative to chloride at a given concentration and for a given cation. Therefore, it was desirable to determine if a corresponding anionic effect could be obtained for the diffusive motions of hydration complexes such that the nitrate ion would restrict their diffusive mobility strongly relative to the chloride anion.

In Fig. 5, the curves of Γ vs. K^2 for 4.3 m $\text{La}(\text{NO}_3)_3$, 4.3 m LaCl_3 , 4.23 m CrCl_3 , and 15.02 m LiCl solutions at 1°C are compared with that for water. In addition, quasi-elastic components observed for the supercooled solutions and the glasses of CrCl_3 and $\text{La}(\text{NO}_3)_3$ are shown, and compared both with the incident energy distribution and with this distribution broadened by the Lorentzian functions with different Γ values. The following features and trends should be noted:

- 1) The curves of Γ vs. K^2 at 1°C for these solutions lie below that for water (a "positive hydration behavior"). Thus, the formation of ion-water hydration complexes (whose characteristic frequencies appear in the inelastic region) decreases the self-diffusion coefficients and increases the residence times relative to water.

- 2) At 1°C , the curves of Γ vs. K^2 for $\text{La}(\text{NO}_3)_3$ and LaCl_3 solutions rise linearly at the origin, and then approach a nearly constant value at the larger values of K^2 , in good accord with a delayed-diffusion model (see Sec. 2A), and show only secondary variations when Cl^- anions are replaced by NO_3^- anions. The weak dependence on anion is contrary to that observed for the glass transitions, which are significantly higher for nitrate solutions than for chloride solutions. This suggested that, in solutions of strongly hydrating cations, the strong anion dependences of the glass transitions might result from other than their influence upon the ordering of H_2O molecules about the cations or upon

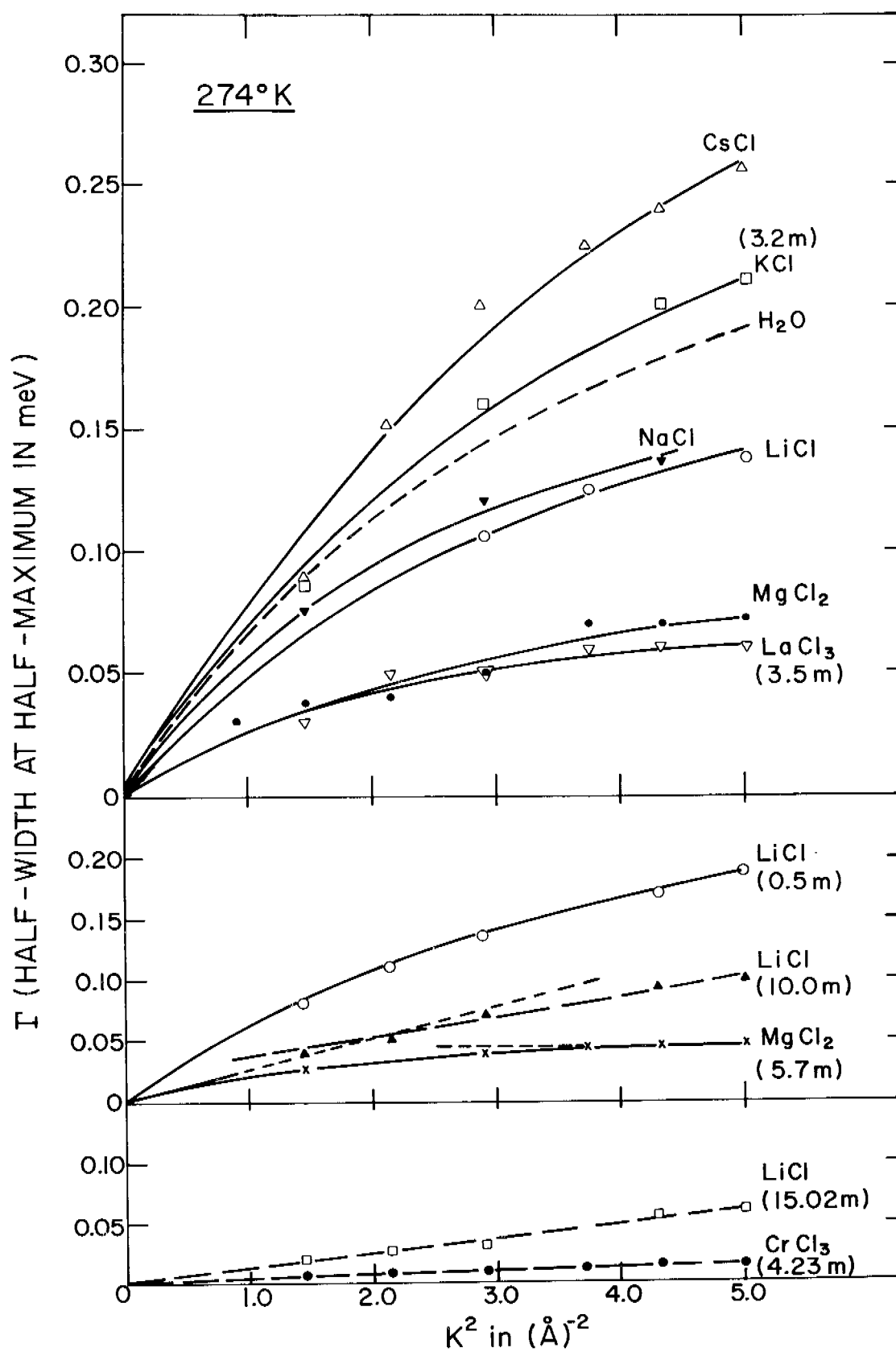


FIGURE 5

The energy distribution of the incident beam, determined by measuring the distribution of neutrons elastically scattered from vanadium, is shown in the lower left graph. This distribution broadened by Lorentzian functions with various half-widths, Γ , as discussed in the experimental section and the main text, are also shown on the same graph.

The quasi-elastic distributions for the supercooled liquid above T_g and for the glass of the 4.23 m CrCl_3 and 4.3 m $\text{La}(\text{NO}_3)_3$ solutions are shown in the upper graph. When compared to the Lorentzian broadened incident distributions, these quasi-elastic distributions have half-width Γ 's below 0.005 meV, which is close to the resolution limit.

In the lower middle graph, Γ 's are plotted as a function of K^2 for several solutions and H_2O at 1°C . The Γ 's for 15.02 m LiCl and 4.23 m CrCl_3 appear to be linear with K^2 , as expected for classical diffusion. The lower right graph contains the plots of Γ vs. K^2 for 4.6 m and 10 m solutions of LiCl and LiNO_3 . The lines were drawn by averaging through the data. For 3.5 m $\text{La}(\text{NO}_3)_3$ and LaCl_3 solutions, the lines are optimum fits to the delayed-diffusion model. The diffusive parameters obtained by the fitting are:

	$D \times 10^5 \text{ cm}^2/\text{sec}$ (From the slope of Γ vs. K^2 near the origin)	$\tau \times 10^{12} \text{ sec}$
3.5 m $\text{La}(\text{NO}_3)_3$	0.5	6.3
3.5 m LaCl_3	0.5	7.9
4.6 m LiNO_3	1.1	2.8
4.6 m LiCl	0.9	3.2

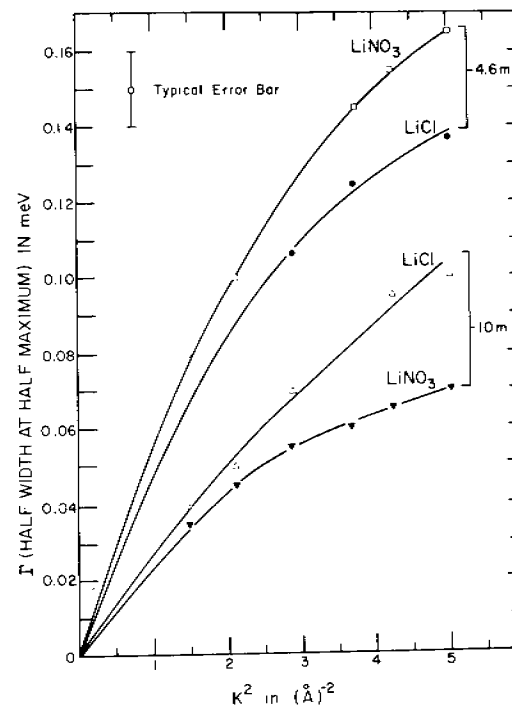
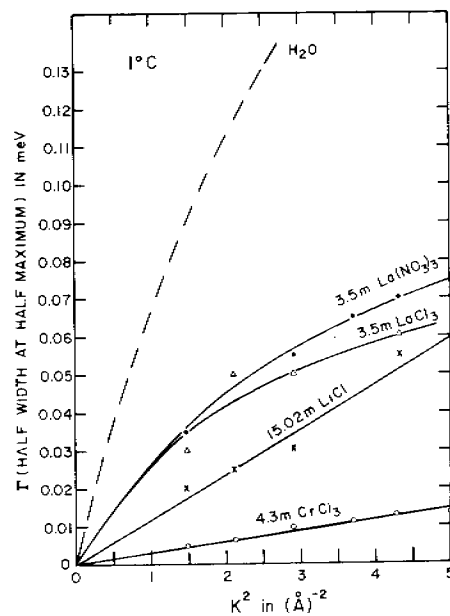
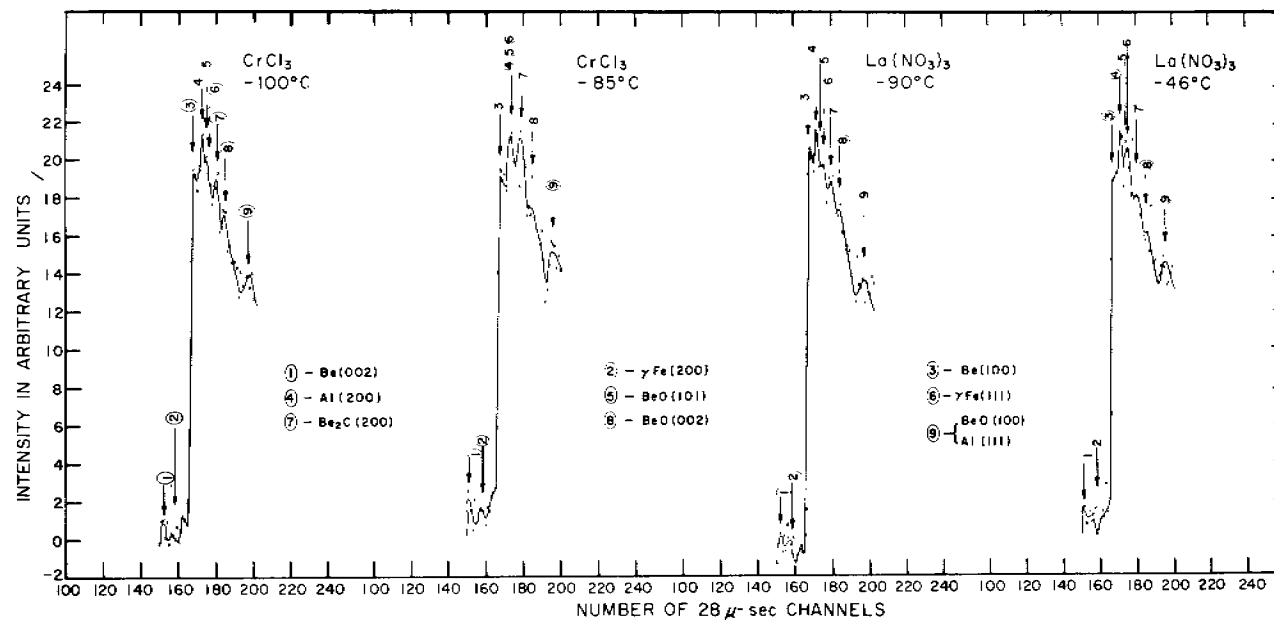
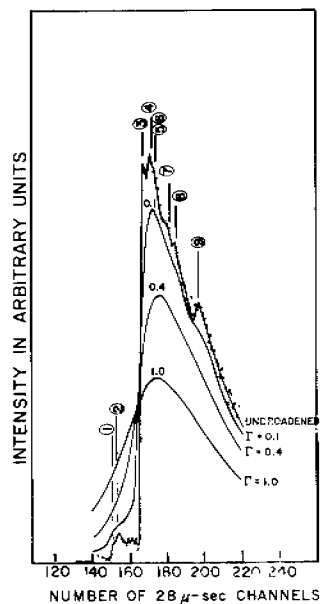


FIGURE 6

The time-of-flight spectra for a CrCl_3 solution at temperatures above and below the glass transition are compared with its solid hydrate. The vertical lines indicate similar frequencies among the spectra. The correspondence between these frequencies and the reported IR frequencies and the frequency distribution are shown in Figure 8.

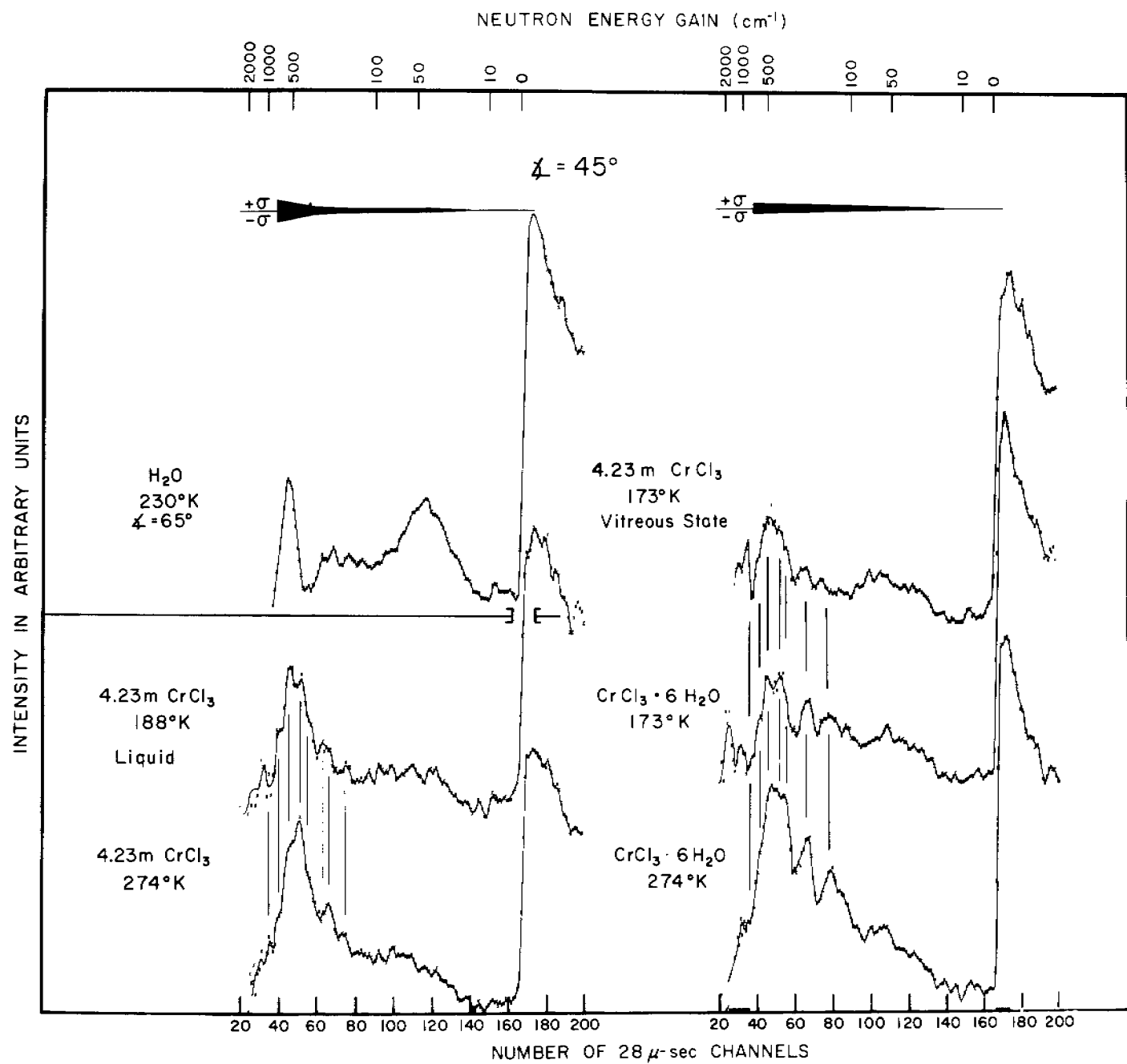


FIGURE 7

The time-of-flight spectra for a $\text{La}(\text{NO}_3)_3$ solution at temperatures above and below the glass transition are compared with its solid hydrate. The vertical lines indicate the similarity in the frequencies. The corresponding frequency distributions for the glasses and supercooled solutions are shown in Figure 8.

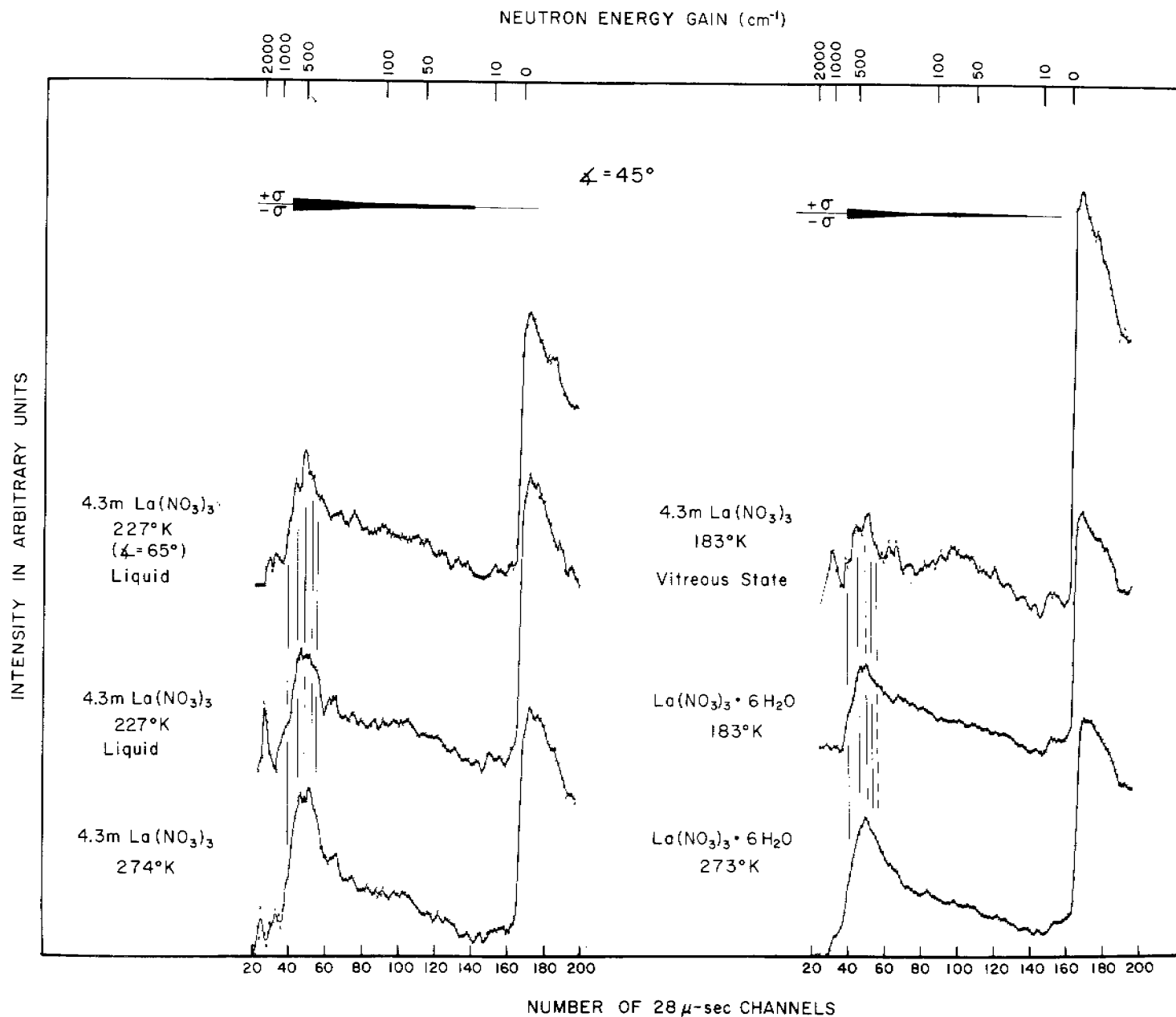


FIGURE 8

The one-phonon frequency distributions calculated from the time-of-flight spectra of CrCl_3 and $\text{La}(\text{NO}_3)_3$ solutions above and below their glass transitions are compared. The spectra shown for CrCl_3 were measured at 173°K (glass) and 188°K (liquid), and the spectra for $\text{La}(\text{NO}_3)_3$ were measured at 183°K (glass) and 227°K (liquid). In order to reduce the size of the graph, the intensity of the right half of each spectrum has been reduced by the factor indicated on the graph. Frequencies enclosed by brackets are reported IR frequencies of the corresponding hydrates. The frequency with the asterisk was calculated from the reported value of the $\text{La}-(\text{OD}_2)$ "rocking" vibration.

A noticeable change in intensity is observed for $\text{La}(\text{NO}_3)_3$ in passing from the glass to the liquid in the region around 160 cm^{-1} where anion-water frequencies occur. This change may be due to the broadening of the liquid spectrum as compared to that of the glass. This change is less noticeable for the CrCl_3 however. In general, the spectra of the glasses exhibit better resolution. Note, for example, the splitting of the frequency which occurs at 554 cm^{-1} in liquid $\text{La}(\text{NO}_3)_3$ into two components (440 cm^{-1} and 600 cm^{-1}) in the spectra of the glass. This and other small shifts cannot be excluded because of experimental resolution and the uncertainty in assigning frequencies.

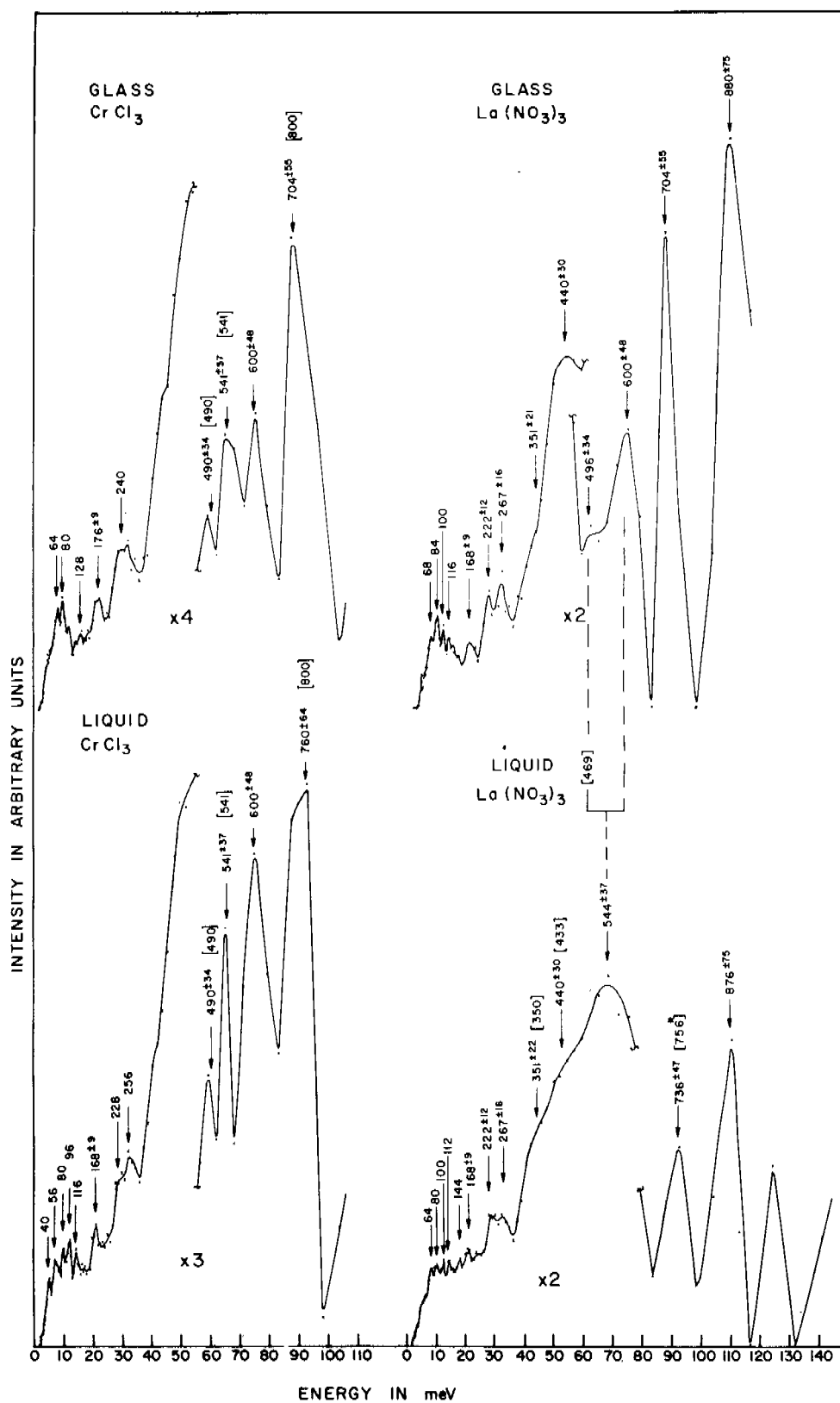


FIGURE 9

The spectra of neutrons scattered at an angle of 45° are compared for a 1.0 m MgCl_2 solution, a 5.7 m MgCl_2 solution, a composite mixture of a 1.0 m MgCl_2 solution and a 4.6 m NaCl solution (assuming simple additivity), a mixture of 1.0 m MgCl_2 and 4.6 m NaCl solutions, and a 4.6 m NaCl solution. The sample temperatures were 1°C . The inelastic maxima corresponding to cation-water frequencies are indicated by solid and dashed lines. A solid line indicates the persistence of such frequencies between two consecutive spectra; a dashed line indicates frequencies that appear in a given spectrum, but are lost or absent in a second spectrum.

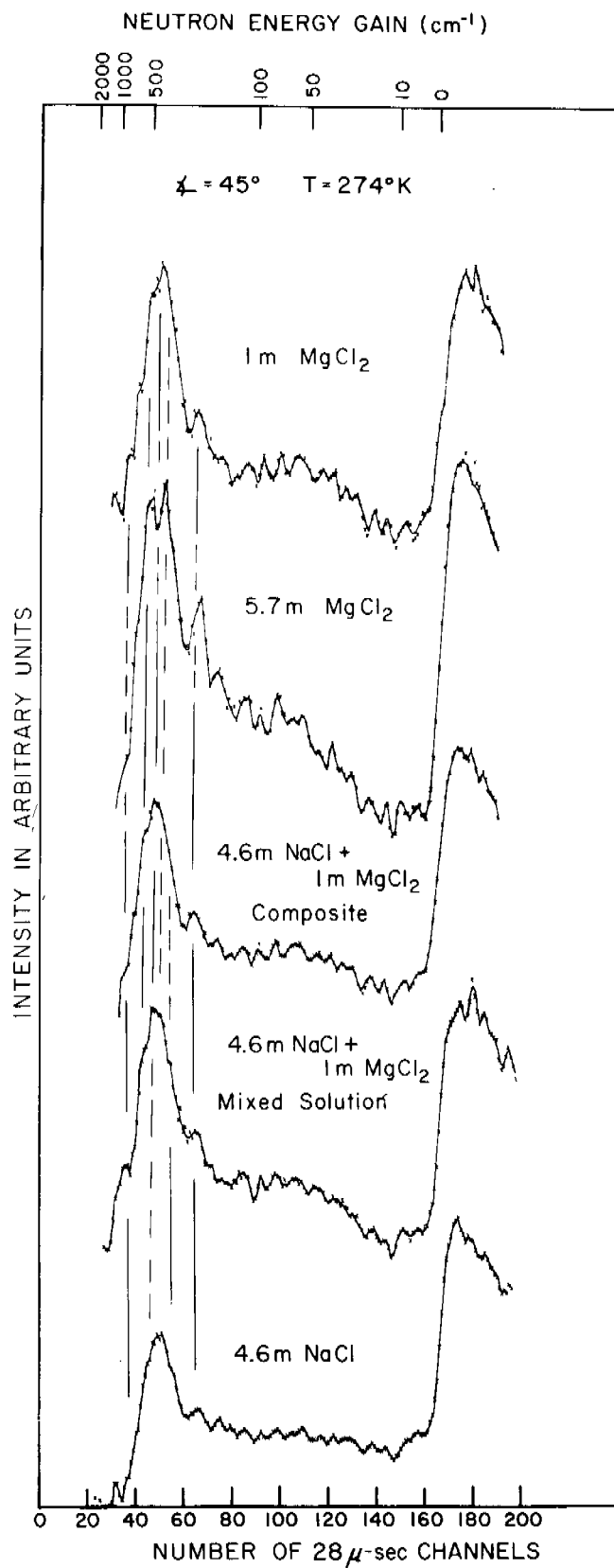


FIGURE 10

The spectra of neutrons scattered at an angle of 45° are compared for a 3.0 m LiCl solution, for a 4.6 m LiCl solution, for a composite spectra of a 4.6 m LiCl solution with a 4.6 m NaCl solution (assuming simple additivity), for the mixture of a 4.6 m LiCl solution with a 4.6 m NaCl solution, and for a 4.6 m NaCl solution. The sample temperatures were 1°C .

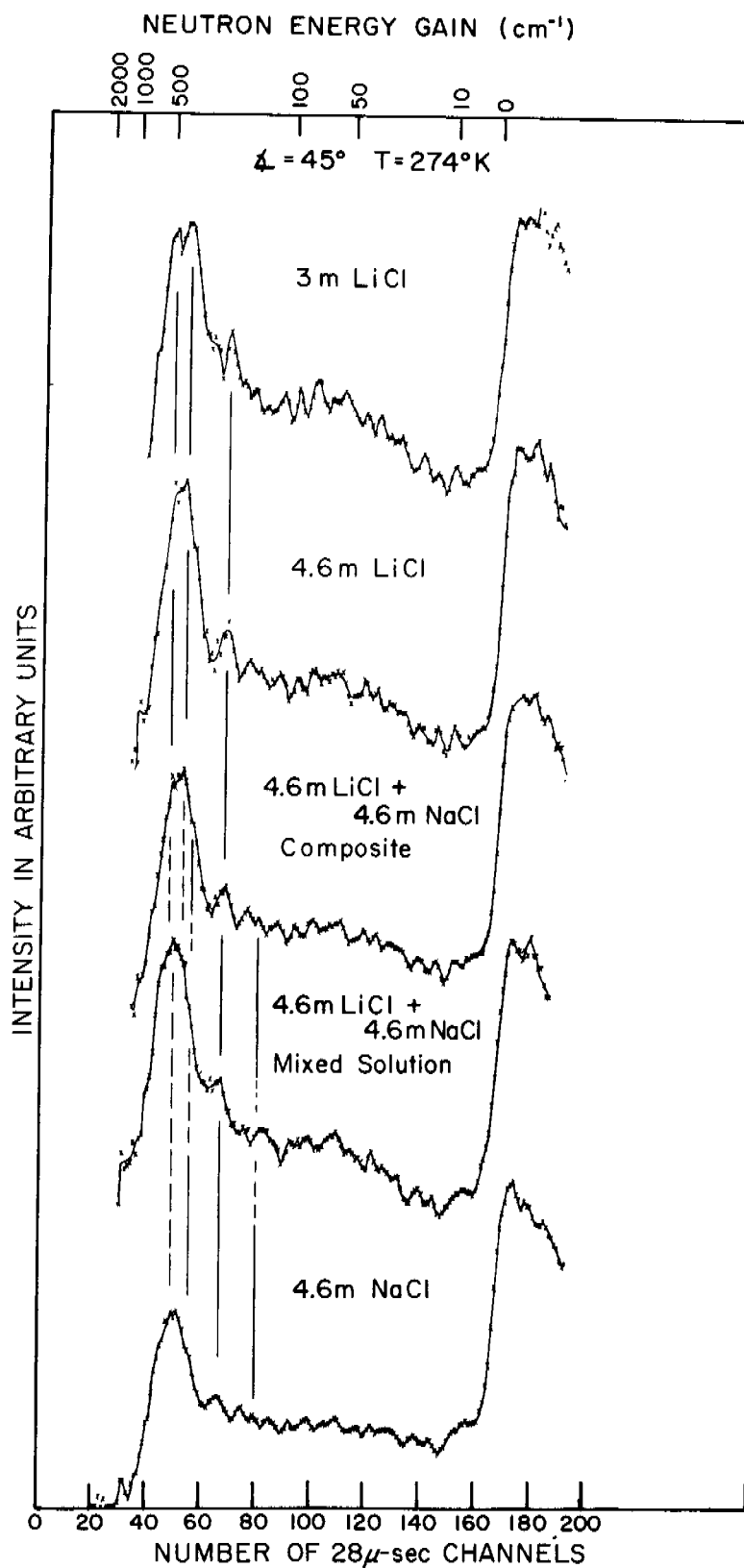


FIGURE 11

The time-of-flight spectra, measured at 1°C, are compared for a 4.6 m NaCl solution, a 4.6 m CsCl solution, a composite spectrum of a 4.6 m NaCl solution and a 4.6 m CsCl solution, and a mixture of 4.6 m NaCl and 4.6 m CsCl solutions. They are also compared with a composite spectrum of 4.6 m NaCl and 4.6 m CsCl solutions measured at 75°C.

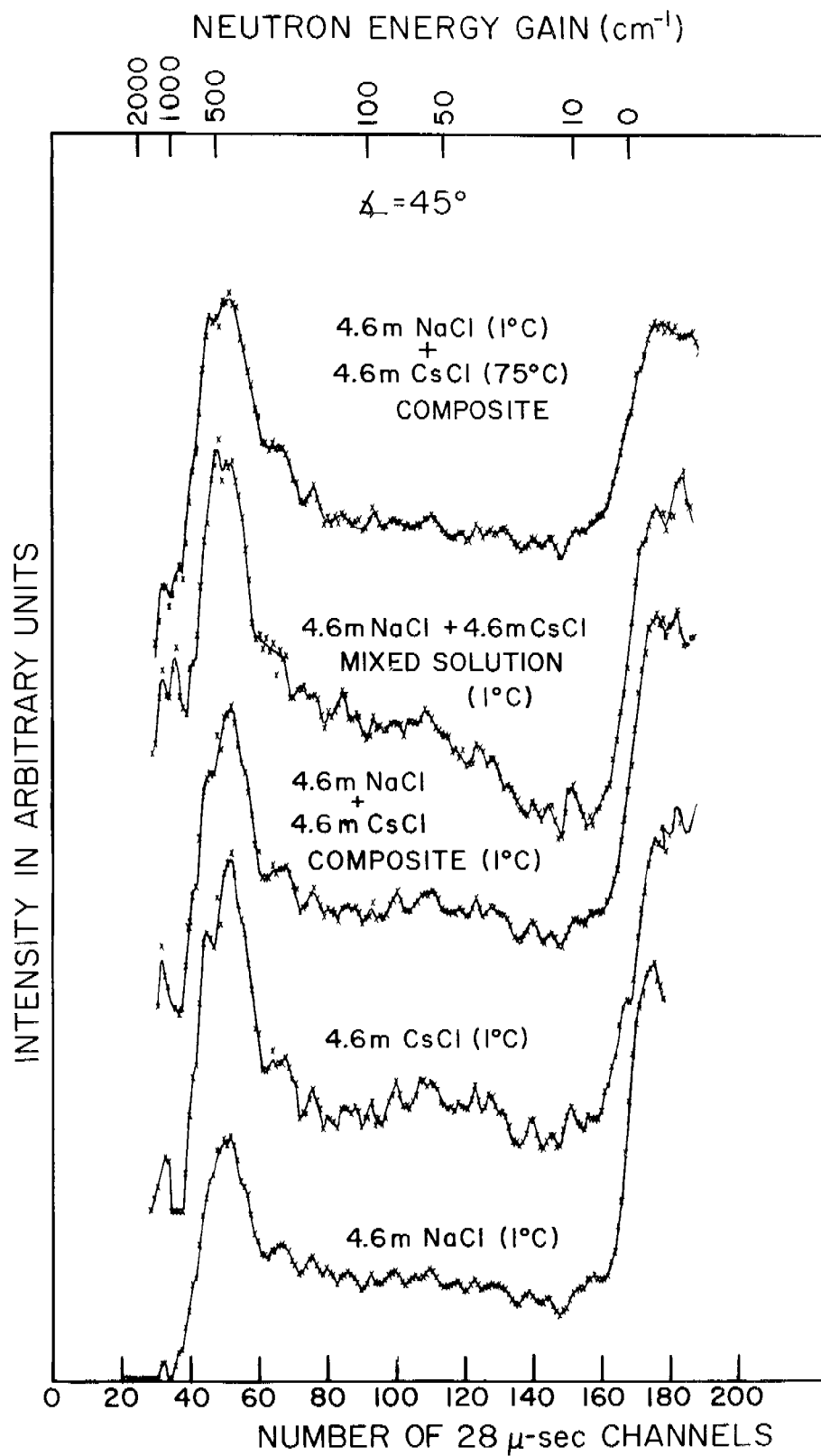


FIGURE 12

The spectra of neutrons scattered at an angle of 45° are compared for a 4.6 m NaCl solution, a 2.2 m MgSO_4 solution, a composite spectrum of a 4.6 m NaCl solution and a 2.2 m MgSO_4 solution (assuming simple additivity), and a mixture of 4.6 m NaCl and 2.2 m MgSO_4 solutions. The sample temperatures were 1°C . The solid lines indicate the persistence of vibrational frequencies between two consecutive spectra.

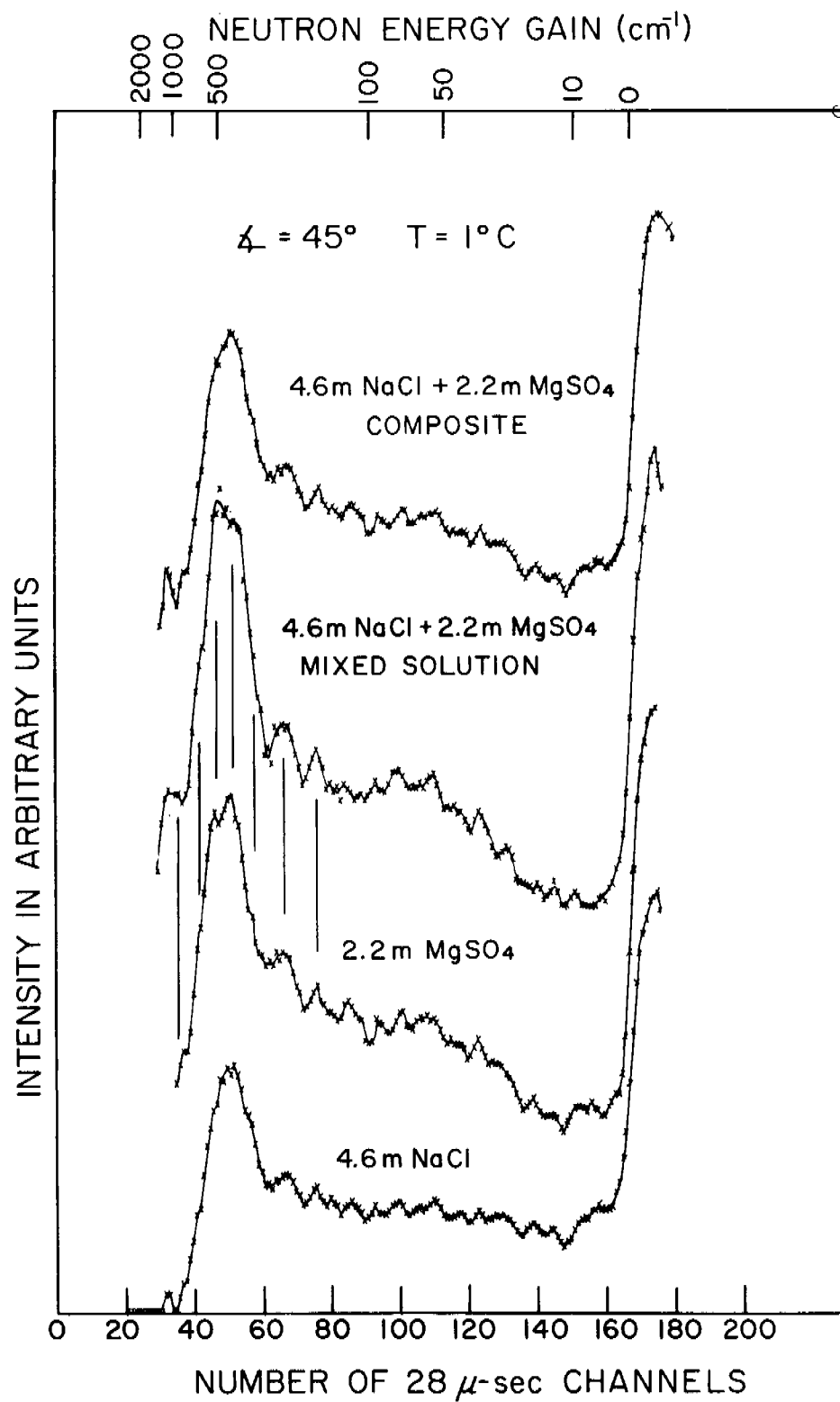


FIGURE 13

The τ vs. K^2 curves for 4.6 m NaCl + 4.6 m LiCl, and 4.6 m NaCl + 1 m MgCl₂ are compared with those of their individual components, as well as with those of their composites, which were calculated by assuming that the activation energy in a mixed solution of two salts would be the simple average of those of their individual solutions.

Temperature = 1°C

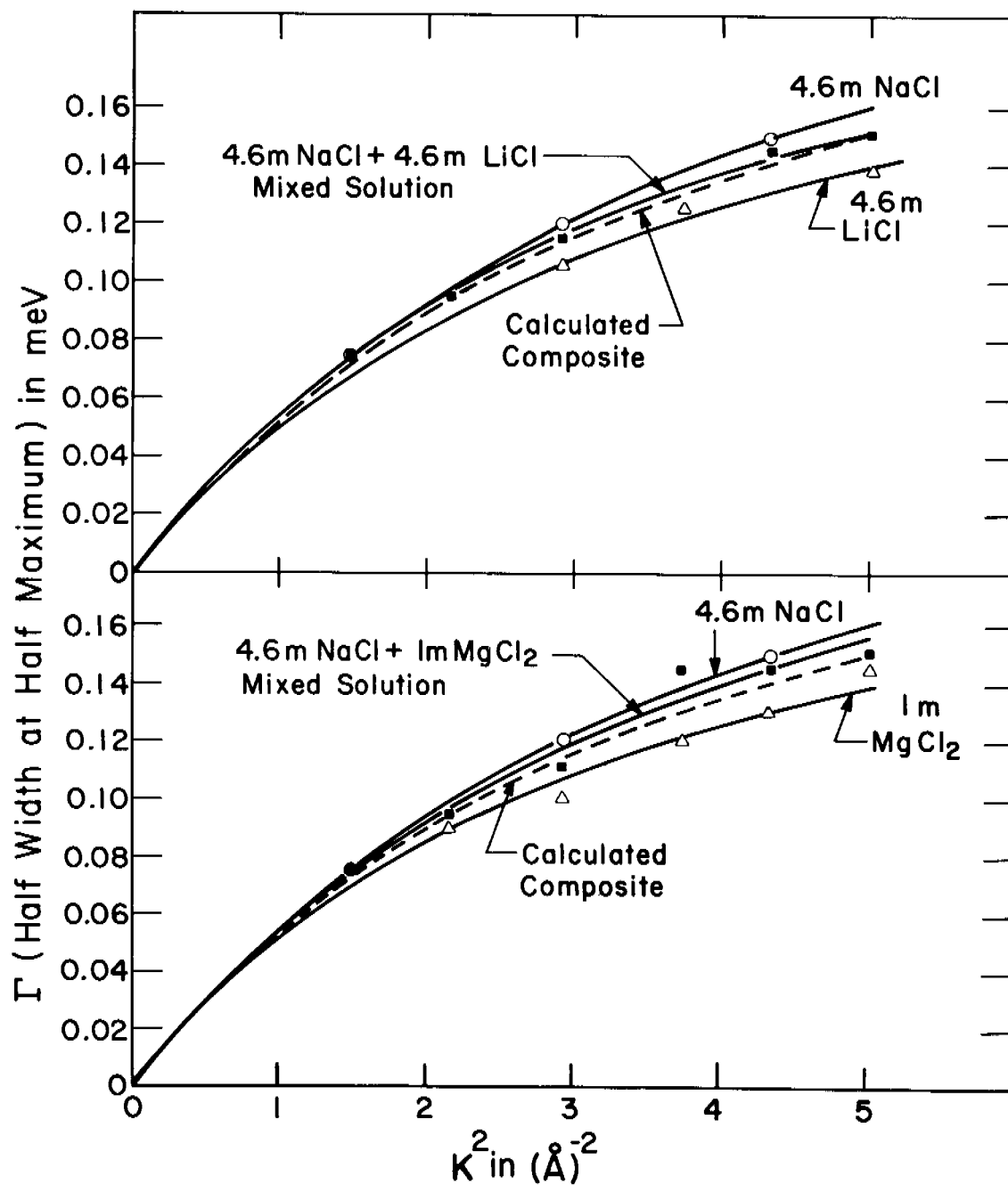
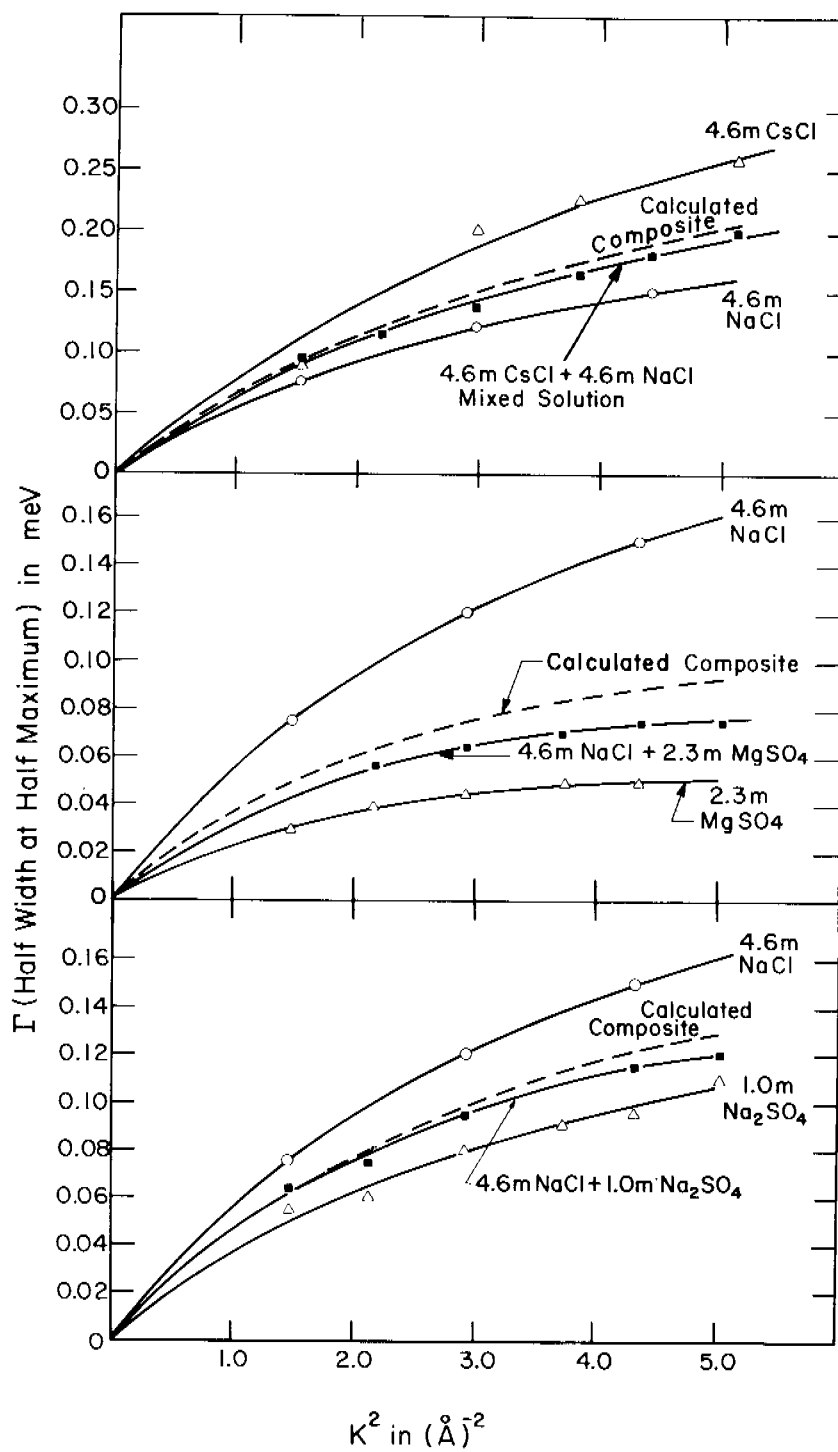


FIGURE 14

The Γ vs. K^2 curves for 4.6 m NaCl + 4.6 m CsCl, 4.6 m NaCl + 2.2 m MgSO₄, and 4.6 m NaCl + 1 m Na₂SO₄ are compared with those of their individual components as well as with those of their composites, which were calculated by assuming that the activation energy in a mixed solution of two salts would be the simple average of those of their individual solutions.

Temperature = 1°C



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